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(54) Title: BORATE CRYSTALS FOR OPTICAL FREQUENCY CONVERSION

(57) Abstract: Novel nonlinear optical materials are described having the general formula $5 M_x M'_y Sc_z (BO_3)_4$ where M and M' are metals, typically rare earth metals, and the sum of x, y, and z is about four. One example of such a material is $La_{0.7}Y_{0.3}Sc_3(BO_3)_4$. Exemplary crystalline materials according to the general formula exhibit useful optical characteristics and desirable physical properties for nonlinear optical applications. Novel compositions and devices using the nonlinear optical materials also are described.

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BORATE CRYSTALS FOR OPTICAL FREQUENCY CONVERSION

CROSS REFERENCE TO RELATED APPLICATION

This application is entitled to the earlier filing date of prior U.S. provisional
5 application No. 60/395,681, filed on July 12, 2002, which is incorporated herein by
reference.

FIELD

This disclosure concerns a novel class of compounds having useful optical
10 properties (e.g., nonlinear optical properties), compositions comprising such
compounds, methods for their manufacture and use, and devices employing such
materials.

BACKGROUND

15 Nonlinear optical (NLO) materials are unusual because their optical
properties are affected by light. For instance, light polarizes certain materials. If the
polarization is linear, then light radiated by the material has the same frequency as
the absorbed light. NLO materials are polarized in a nonlinear manner. As a result,
the frequency of the light produced by a nonlinear optical material is some value
20 times the frequency of the light incident on the material.

Laser technology has benefited from the development of new NLO materials.
However, known NLO materials often are suitable only for those applications for
which they were particularly designed. As a result, new NLO materials continually
must be developed having properties selected for a particular application.

25 Among known NLO crystals, borates of the type LiB_3O_5 and BaB_2O_4 are
commercially important, at least in part, because they generate high-power laser
light. LiB_3O_5 crystals have been used in patented devices. For example, Chuangtian
et al.'s U.S. Pat. No. 4,863,283 describes an NLO device that uses a single LiB_3O_5
crystal. While LiB_3O_5 is widely used to convert near infrared light into visible light,
30 it has an insufficient birefringence to allow direct second-harmonic generation of
UV light. Thus, applications using LiB_3O_5 generally have been limited to selected
wavelengths. In contrast, BaB_2O_4 exhibits a birefringence that is sufficient for UV

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generation, but its small angular acceptance limits general applicability.

The material $\text{CsLiB}_6\text{O}_{10}$ (Keszler, U.S. Patent No. 5,684,813, incorporated herein by reference; Sasaki et al. U.S. Pat. No. 6,296,784) has an intermediate birefringence to that of LiB_3O_5 and BaB_2O_4 , and is well suited for high-power UV
5 generation. Unfortunately, $\text{CsLiB}_6\text{O}_{10}$ is an extremely hygroscopic material that is difficult to manufacture; as a result, it has achieved only limited commercial success.

Another borate crystal, $\text{Sr}_2\text{Be}_2(\text{BO}_3)_2\text{O}$ (Chuangtian et al. U.S. Pat. No. 5,523,026), has been promoted for generating short-wavelength light. To date,
10 crystals of this material have not been grown with sufficient size and purity to demonstrate commercial viability.

Recently, $\text{KBe}_2\text{BO}_3\text{F}_2$ crystals have been used to generate wavelengths shorter than 200 nm [see Tagashi, *et al.* Optics Letters 2003, 28(4), 254-256]. However, $\text{KBe}_2\text{BO}_3\text{F}_2$ has not been grown to commercially acceptable sizes, and it
15 is too soft to be reliably cut and polished.

Doped and undoped materials known prior to the present application having the general formula $(\text{La,Ln})\text{Sc}_3(\text{BO}_3)_4$ (Ln = lanthanide) generally crystallize in the space groups Cc, C2/c, or C2. These latter groups commonly have been associated with the laser material $\text{Nd:LaSc}_3(\text{BO}_3)_4$. See, Li, Yunkui; Aka, G.; Kahn-Harari, A.; Vivien, D.; Phase Transition, Growth, and Optical Properties of $\text{Nd}_x\text{La}_{1-x}\text{Sc}_3(\text{BO}_3)_4$
20 Crystals, *J. Mater. Res.* 2001, 16, 38-44. Despite numerous studies reported in the technical and patent literature concerning $\text{Nd:LaSc}_3(\text{BO}_3)_4$, apparently no one previously considered using these materials for nonlinear optical applications involving the production of UV and VUV light. The literature primarily addresses
25 using $\text{Nd:LaSc}_3(\text{BO}_3)_4$ as a laser material. Certain compounds belonging to the same series of materials also have appeared in the Russian-language literature. See, Kuz'micheva, G. M.; Rybakov, V. B.; Novikov, S. G.; Ageev, A. Yu; Kutovoi, S. A.; Kuz'min, O. V.; Zhurnal Neorganicheskoi Khimii; Disordered Structures of Rare Earth Scandoborates of the Huntite Family, 1999, 44(3), 352-366, incorporated
30 herein by reference.

Known NLO compounds are limited in their application to generation of UV and VUV light, are damaged by exposure to high-power lasers, exhibit excessive

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absorption and light scattering of incident or absorbed light, and/or are too costly and time consuming for commercial production. As a result, there is a continuing need for new NLO compounds, methods for their manufacture, crystallization, and use.

5

SUMMARY

The present disclosure concerns a material, particularly a nonlinear optical material, according to Formula 1.



10

Formula 1

With reference to Formula 1, the sum of x, y, and z is about four, and M and M' preferably are selected from the group consisting of La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y. Particularly useful metals are independently selected from the group consisting of Y, Pr, Gd, Yb and Lu.

15

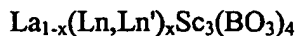
A second embodiment of the present disclosure is more particularly directed to a nonlinear optical material according to Formula 2.



Formula 2

20 With reference to Formula 2, each of x, y, and z is greater than zero, and the sum of x, y and z is about four. M is selected from the group consisting of rare earth metals if y is greater than 0.3, or is selected from the group of rare earth metals other than Nd, including La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y.

25 A third embodiment of the present disclosure concerns a nonlinear optical material where metal M of Formula 2 is a mixture of rare earth metals, i.e., such compounds have mixed stoichiometries (Ln and Ln') indicated by Formula 3.

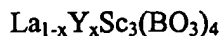


Formula 3

30 With reference to Formula 3, x is greater than zero and less than one. Ln and Ln' are independently selected from the group of rare earth metals, such as La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y, with particularly useful metals for Ln and Ln' being independently selected from the group consisting of Y, Pr, Gd, Yb and Lu.

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A fourth embodiment of the present disclosure concerns a nonlinear optical material according to Formula 4.



Formula 4

- 5 With respect to Formula 4, x is greater than zero and less than one. Typically, x varies from about 0.2 to about 0.4, and currently preferred compounds have x vary from about 0.25 to about 0.35. One example, without limitation, of a compound satisfying Formula 4 is $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$.

The present disclosure also is directed to compositions comprising a material
10 or materials according to Formulas 1-4. Such compositions can include, for example, and without limitation: combinations of materials satisfying Formulas 1-4; a first nonlinear optical material according to any of Formulas 1-4 in combination with another material or materials that facilitate optical applications, whether such material or materials are optical materials (e.g., laser or NLO materials) or not; and
15 at least a first material satisfying Formulas 1-4, and at least a second nonlinear optical material known prior or subsequent to the present disclosure, with or without a laser material.

A method for crystallizing NLO materials disclosed herein also is described. The method generally comprises forming a trigonal phase from a flux comprising
20 lithium borate and yttrium oxide. In a working embodiment, the flux was formed using Li_2CO_3 , B_2O_3 and Y_2O_3 in an approximate ratio of 16:11:1. A mixture is formed comprising the flux and a first compound for crystallization, such as a compound satisfying any of Formulas 1-4. Generally, the mixture is heated to a temperature sufficient for melting. Working embodiments typically have heated the
25 mixture to a temperature of about 1,350 K. An oriented seed crystal is added to the melt, and the melt with seed crystal is then cooled at a cooling rate suitable to initiate crystal growth. Crystal growth is continued until a desired crystal size is obtained.

Further embodiments of the disclosure concern devices that employ
30 nonlinear optical materials. One such device is, without limitation, an optical parametric oscillator (OPO). An OPO uses NLO materials to produce widely tunable coherent light. Optical devices of the present invention comprise a light

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source, such as a laser, optically coupled to nonlinear optical materials described herein or combinations thereof. Such devices may be used to generate UV light, VUV light or both.

5 **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a structural drawing of a compound having the formula $M_xM'_ySc_z(BO_3)_4$.

FIG. 2 is a phase matching curve of particle size (μm) versus intensity (second harmonic generation intensity) for crystals of materials described herein,
10 with a fundamental wavelength of 1064 nm and a generated wavelength of 532 nm.

FIG. 3 is a cleaved portion of a yttrium-lanthanum, scandoborate (YLSB) boule.

FIG. 4 is a transmission spectrum for YLSB crystals [wavelength (nm) versus transmission (%)].

15

DETAILED DESCRIPTION

I. General Molecular Formulas

Disclosed embodiments of the present class of compounds typically satisfy Formula 1

20 $M_xM'_ySc_z(BO_3)_4,$

Formula 1

where M and M' are metals and the sum of x, y, and z is about four. M and M' typically are rare earth metals and combinations of rare earth metals. The rare earth metals are defined herein to include the lanthanides (elements 57-71), scandium and
25 yttrium. M and M' preferably are independently selected from the group consisting of La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y, and are more typically independently selected from the group consisting of La, Pr, Dy, Ho, Er, Yb, Lu, Sc and Y. Particularly useful metals are independently selected from the group consisting of Y, Pr, Gd, Yb and Lu. However, with reference to Formula 1,
30 where one of M or M' is Ce, then the remaining metal is other than Gd or Nd. And if one of M or M' is La, then the remaining metal is other than Nd, or x is greater than 0.3. Structural variations are observed for this family, depending on the

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identity of the rare earth metals selected.

A second embodiment of the present disclosure is directed more particularly to a nonlinear optical material according to Formula 2.



5 **Formula 2**

With reference to Formula 2, each of x, y, and z is greater than zero, and the sum of x, y and z is about four. M is selected from the group consisting of rare earth metals if y is greater than 0.3, or is selected from the group of rare earth metals other than Nd, including La, Pr, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y. Particular
10 embodiments of M are selected from the group consisting of Y, Pr, Gd, Yb and Lu, and combinations thereof.

A third embodiment of the present disclosure concerns a nonlinear optical material where metal M of Formula 2 is a mixture of rare earth metals, i.e., such compounds have mixed stoichiometries (Ln,Ln') indicated by Formula 3.



Formula 3

With reference to Formula 3, x is greater than zero and less than one, and more typically x varies from about 0.2 to about 0.4, with currently preferred compounds having x vary from about 0.25 to about 0.35. Ln and Ln' independently are selected
20 from the group of rare earth metals, such as La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y, and are more typically independently selected from the group consisting of La, Pr, Gd, Dy, Ho, Er, Yb, Lu, Sc and Y. Particularly useful metals for Ln and Ln' are independently selected from the group consisting of Y, Pr, Gd, Yb and Lu.

25 Using the general synthesis described herein, selected samples of the mixed stoichiometries $\text{La}_{1-x}(\text{Ln,Ln}')_x\text{Sc}_3(\text{BO}_3)_4$ satisfying Formula 3 have been prepared. For example, compounds where Ln = Y and Ln' = Dy, Ho, and Er have been made. X-ray powder diffraction measurements and second-harmonic tests establish that the samples crystallize in the R32 space group. Refined unit-cell parameters are
30 provided below in Table 1.

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Table 1

$\text{La}_{0.7}\text{Y}_{0.15}\text{Ln}_{0.15}\text{Sc}_3(\text{BO}_3)_4$		
	Cell Parameters for R32 Materials	
Ln	a	c
Dy	9.77	8.00
Ho	9.77	8.00
Er	9.81	7.97

A fourth embodiment of the present disclosure concerns a nonlinear optical material according to Formula 4.



Formula 4

With respect to Formula 4, x is greater than zero and less than one. Typically, x varies from about 0.2 to about 0.4, and currently preferred compounds have x varying from about 0.25 to about 0.35. One example, without limitation, of a
 10 compound satisfying Formula 4 is $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$.

A. Space Group

Materials suitable for NLO applications often crystallize in a particular space group, such as the R32 space group. As a result, claimed compounds include, but
 15 are not limited to, those satisfying any of Formulas 1-4 crystallized in the R32 space group. A particular example of such a compound is $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$ crystallized in the R32 space group.

Prior to the present disclosure, the stabilization and growth of a widely transparent R32 form of the general formula $\text{M}_x\text{M}'_y\text{Sc}_z(\text{BO}_3)_4$ had not been
 20 demonstrated. $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$ appears to be the first example of such a compound. It is unique among all of the $\text{MSc}_3(\text{BO}_3)_4$ compounds in that it forms as a mixture of two rare earth metal atoms, La and Y, within a narrow composition range. The results of an X-ray diffraction study of the material, which establishes the structure of the compound, are summarized in Tables 2 and 3 below.

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Table 2
Crystallographic data for $\text{La}_{0.75}\text{Y}_{0.25}\text{Sc}_3(\text{BO}_3)_4$.

5	Parameter	Value/Property
	Formula Weight, amu	496.51
	Crystal System	Rhombohedral
	Space Group	R32(h) [155]
	a , Å	9.805(3)
10	c , Å	7.980(2)
	V , Å ³	664.4(2)
	Z	3
	D_{calc} , g cm ⁻³	3.722
	$F(000)$	695
15	Diffractometer	Rigaku AFC6R
	Radiation	Mo K α ($\lambda=0.71069$) graphite-monochromated
	Data Collection	$\pm h, k, \pm l$
	No. Observations (total, unique)	2065, 380
20	($F_o^2 \geq 3\sigma(F_o^2)$)	380
	R	0.022
	R_w	0.031
	Maximum Shift in Final Cycle	0.00
	GOF	1.07
25	$R = \Sigma F_o - F_c / \Sigma F_o = 0.022$ $R_w = [(\Sigma w (F_o - F_c)^2 / \Sigma w F_o^2)]^{1/2} = 0.031$	

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Table 3
Positional and thermal parameters (B_{eq}) and occupancy for
 $La_{0.75}Y_{0.25}Sc_3(BO_3)_4$.

Atom	Wy	x	y	z	B_{eq}^a
La ^b	3a	0	0	0	0.79(1)
Sc	9d	0.4572	0	0	0.56(2)
B(1)	3b	0	0	½	0.67(8)
B(2)	9e	0.5507(5)	0	½	0.72(6)
O(1)	9e	0.1405(4)	0	½	0.80(4)
O(2)	18f	0.5449(4)	0.8580(4)	0.4853(4)	1.16(4)
O(3)	9e	0.4081(5)	0	½	1.53(7)

^a $B_{eq} = (8\pi/3)^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

^boccupancy = 0.154/0.1667, remainder of site is occupied by Y as demonstrated by electron microprobe analysis

The nonlinear signal of $La_{0.7}Y_{0.3}Sc_3(BO_3)_4$ is approximately 0.67 times that of the NLO material BaB_2O_4 . Furthermore, the high birefringence of the material provides a means for angular phase matching to produce UV and VUV wavelengths, in addition to broadly tunable radiation of both short and long wavelengths in OPO wavelengths. Thus, materials having the general formula $M_xM'_ySc_z(BO_3)_4$, particularly $La_{0.7}Y_{0.3}Sc_3(BO_3)_4$, exhibit all of the characteristics in terms of optical and physical properties, as well as stability and manufacturability, that are necessary for a commercially successful NLO material.

Additional useful NLO materials according to general Formula 1, i.e., $M_xM'_ySc_z(BO_3)_4$, can be selected from the group consisting of those having M and M' independently selected from the group consisting of La, Y, Lu, Yb, and Pr. Examples of such compounds include, without limitation, $Pr_{1-x}Y_xSc_3(BO_3)_4$, $Pr_{1-x}La_xSc_3(BO_3)_4$, and $La_{1-x}Lu_xSc_3(BO_3)_4$.

Representative compounds having Formulas 1, 2, 3 and/or 4 have been made according to the general synthetic methodology discussed herein, including without limitation those compounds indicated by Table 4 below. If a mixture of phases is obtained, a substantially pure sample of the desired NLO phase can be obtained using the crystallization procedure described herein.

Table 4

Composition			Phases
Y	La	Sc	
0.1	0.9	3	LSB
0.15	0.85	3	YLSB+LSB
0.2	0.8	3	YLSB+LSB
0.25	0.75	3	YLSB + LSB?
0.25	0.75	3	YLSB+LSB
0.25	0.75	3	YLSB+LSB
0.3	0.7	3	YLSB+LSB
0.35	0.65	3	YLSB+ScBO3
0.35	0.65	3	YLSB
0.35	0.65	3	YLSB+ScBO3
0.37	0.63	3	YLSB+ScBO3
0.39	0.61	3	YLSB+ScBO3
0.4	0.6	3	YLSB+ScBO3
0.41	0.59	3	YLSB+ScBO3
0.45	0.55	3	YLSB+ScBO3
0.5	0.5	3	YLSB+ScBO3+Sc2O3
0.65	0.35	3	YLSB+ScBO3+Sc2O3
0.7	0.3	3	YLSB+ScBO3
0.8	0.2	3	YLSB+ScBO3+Sc2O3
Dy.05	0.95	3	LSB+DyLSB?
Dy.1	0.9	3	LSB+DyLSB?
Dy.2	0.8	3	LSB+DyLSB?
Dy.3	0.7	3	DyLSB
Dy.4	0.6	3	DyLSB+DyBO3
Yb.25	0.75	3	LSB+YbLSB
Yb.25	1	2.75	LSB+Yb2O3?

II. Compositions Comprising NLO Materials

- 5 The present disclosure also is directed to compositions comprising a material or materials according to Formulas 1-4. Such compositions can include combinations of materials satisfying Formulas 1-4. A first nonlinear optical material according to any of Formulas 1-4 also can be used in combination with another material or materials that facilitate optical applications, whether such materials are
- 10 optical materials (e.g., laser or NLO materials) or not. For example, a first nonlinear optical material according to any of Formulas 1-4, or combinations of species satisfying Formulas 1-4, may be operatively associated with a second laser material. In another embodiment, a composition may include two or more materials, such as a first material according to Formulas 1-4, with a second material that does not

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operate as an optical material, but otherwise facilitates using compounds of the present disclosure. In yet another embodiment, the compositions may include at least a first material satisfying Formulas 1-4, and a second, known nonlinear optical material, with or without a laser material.

5 The compositions can be formed by methods currently known or hereafter developed. For example, physical mixtures of compounds may be formed by physically combining desired quantities of two or more materials. Alternatively, compositions may be formed by operatively coupling materials one to another, such as by joining materials by a method such as diffusion bonding (see the discussion of
10 diffusion bonding in, for example, Meissner's U.S. patent No. 5,441,803, which is incorporated herein by reference) or other suitable method.

III. General Method for Making NLO Materials

 A number of techniques, currently known or hereinafter developed, can be
15 used to synthesize compounds that satisfy Formulas 1-4. In general, and without limitation, compounds satisfying the general formulas have been synthesized by heating appropriate molar amounts of starting materials to a temperature sufficient to form the nonlinear optical materials.

 More particularly and with reference to working embodiments, appropriate
20 starting materials and amounts thereof were selected and ground to a powder in a mortar and pestle. A mixture was then formed by combining the powdered starting materials together in appropriate molar amounts. The mixture was then heated, such as in a crucible, to a temperature sufficient to form desired compounds, preferably as a single-phase. Working embodiments typically were heated to a temperature of
25 about 1,000° C.

 Crystals were then allowed to grow from a flux melt. Transparent crystals of nonlinear optical materials were obtained by this process. The method for growing crystals satisfying Formulas 1-4 involves forming a trigonal phase from a lithium-borate, yttrium-oxide flux. Working embodiments formed this flux using
30 substantially pure Li_2CO_3 , B_2O_3 and Y_2O_3 in an approximate weight ratio of 16.66:11.11:1. Material to be crystallized was mixed with the flux material, and then heated to a temperature sufficient to melt the desired compound. Working

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embodiments have heated the mixture comprising flux and desired NLO material to a temperature of about 1,350 K. The flux is held at this temperature, or at least a temperature above the melting temperature, for a period of time, referred to as a "soak time," that is sufficient to provide a uniform melt composition. Working
5 embodiments have used soak times of about 48 hours. An oriented seed crystal is added to the mixture, and the mixture cooled at a suitable rate to initiate crystal growth, such as a cooling rate of about 2K/day. Crystal growth is continued until a desired crystal size is obtained, and then the flux material is removed. Flux material is initially removed first by physical methods. Residual flux material attached to the
10 crystal is removed by dissolution in strong acid, particularly a strong mineral acid, such as nitric acid.

IV. Nonlinear Optical Material Applications

Devices using nonlinear optical materials are known. Such devices can be
15 used, without limitation, for direct second-harmonic frequency conversion of laser light to visible, UV, and VUV wavelengths. Further uses of nonlinear optical materials in devices include frequency mixing, including sum and difference frequency mixing of laser light to yield light having a wavelength selected from the group consisting of infrared, visible, UV, and VUV wavelengths.

20 A further application of the current nonlinear optical materials uses the materials in a system, such as a monoblock laser system. Systems can be fabricated using a composite containing the current nonlinear optical materials. Such composites can contain a first material according to any of Formulas 1-4, and a second material. The first material and the second material can be diffusion bonded
25 or joined by another suitable method. Where the second material is a laser material, the nonlinear optical material can be oriented for angular phase matching and generation of the second harmonic of the laser.

A second system that can exploit nonlinear optical materials can be fabricated using two nonlinear optical materials and a laser material. The nonlinear
30 optical materials can be the same or different materials, and one or both can be selected from crystals having any of general Formulas 1-4. A first nonlinear optical material can be joined to a laser material by diffusion bonding, or other suitable

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method, and the nonlinear material can be oriented for angular phase matching of the second harmonic of the laser. A second nonlinear optical material can be joined to the first by a similar suitable method, such as diffusion bonding. The second nonlinear optical crystal can be oriented to yield, in conjunction with the first
5 material, the fourth harmonic of the laser.

Further details concerning NLO materials, methods for their use, and devices utilizing such compounds, are described in Keszler's U.S. Patents, Nos. 5,684,813, 5,677,921, 6,417,954, 6,441,949, and 6,500,364, which are incorporated herein by reference.

10

V. Working Examples

The following examples describe particular embodiments concerning the presently disclosed technology. These examples should be interpreted as illustrative with respect to particularly described embodiments only, and such examples are not
15 intended to limit the invention to the specific features detailed therein. Thus, it should be understood that additional embodiments not limited to these particular features described are consistent with the following examples.

Example 1

20 This example describes the synthesis of $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$. Lanthanum oxide (La_2O_3 , 23.08 wt%, dried overnight in a drying oven), scandium oxide (Sc_2O_3 , 41.87 wt%), yttrium oxide (Y_2O_3 , 6.86 wt%) and boron oxide (B_2O_3 , 28.19 wt%) were ground in a mortar and pestle. LiBO_2 [0.05 x weight $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$, e.g., about 0.2 g] was added and the mixture ground for 5 minutes. The ground material
25 was transferred to a platinum crucible, covered, and heated in a furnace at 1 °C per minute, to 1,050 °C. The material was held at this temperature for 2 hours, and then allowed to cool at 0.1 °C per minute. The material was then removed from the furnace and allowed to cool to room temperature. Several plate-like crystals were fractured from the material for X-ray crystallographic analysis.

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Example 2

This example describes how the nonlinear optical materials described above can be used to generate second harmonic light energy. A Nd:YAG laser is used as a light source to generate 1064-nm light. This light is filtered and passed through a sample of NLO material prepared according to Example 1 and mounted on a silica glass plate. Second harmonic light energy emerges from the NLO crystal and is directed onto a photomultiplier tube to a dichroic mirror. The light energy may be monitored by an oscilloscope.

10

Example 3

This example describes a method for growing crystals of materials described herein. This particular example is directed to growing crystals of $Y_xLa_{1-x}Sc_3(BO_3)_4$, $x = 0.2-0.4$ (YLSB).

YLSB crystals have been grown by a high-temperature, top-seeded solution method. Lithium borate, $xLi_2O \cdot yB_2O_3$, was used as the flux, and extra Y_2O_3 was added to obtain the desired trigonal phase. A typical mixture for crystal growth was 1 $Y_{0.3}La_{0.7}Sc_3(BO_3)_4$, 0.45 Y_2O_3 (Stanford Materials, 99.999%), 7.5 Li_2CO_3 (Cerac, 99.99%) and 5 B_2O_3 (Cerac, 99.9%). The mixture was heated in a platinum crucible to 1,350 K and soaked for two days. An oriented seed was used to initiate growth and to determine the initial growth temperature. Crystals have been grown by cooling at a rate of 2K/day; crystal growth was continued until the desired boule size was obtained - typically 30 x 30 x 10 mm. Colorless, transparent crystals with natural facets have been produced with this method. The crystals are stable to water and acid, and hence the flux attached to the crystal can be readily dissolved in nitric acid.

25

Example 4

This example concerns determining second-harmonic generation of light using crystals of materials described herein, such as the crystals described in Example 3. Phase-matched, second-harmonic generation of 532-nm light is observed by appropriately orienting the grown crystals in a 1064-nm laser beam. This phase-matched operation is also evident from measurements made on ground

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- 15 -

crystals, wherein the second-harmonic signal is monitored as a function of particle size. As shown in FIG. 2, the shape of the curve is consistent with phase-matched behavior

Portions of the YLSB boules have been used (see FIG. 3) to determine
5 transparency in the UV portion of the spectrum. The crystals exhibit preferred cleavage, and are mechanically robust and sufficiently hard to be readily polished. As shown in FIG. 4, the crystals exhibit high transparency in the UV portion of the spectrum. The high-energy, short-wavelength absorption cut-off has not been explicitly determined, since the loss of signal near 190 nm largely represents the
10 wavelength limit of the spectrometer.

The present invention has been described with reference to preferred embodiments. Other embodiments of the invention will be apparent to those of ordinary skill in the art from a consideration of this specification, or practice of the invention disclosed herein. It is intended that the specification and examples be
15 considered as exemplary only, with the true scope and spirit of the invention being indicated by the appended claims.

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Appendix

The following references describe materials useful for optical applications, and applications of such materials. Each of the following documents is incorporated herein by reference:

- 5 1. Lin, ZhouBin; Hu, ZuShu; Han, XiuMei; Zhang, LiZhen; Wang, GuoFu. **Spectral parameters of Nd³⁺ ion in λ -Nd³⁺: LaSc₃(BO₃)₄ crystal.** *Physica Status Solidi B: Basic Research* (2002), 231(2), 607-612.
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- 20 12. Goryunov, A. V.; Kuz'micheva, G. M.; Mukhin, B. V.; Zharikov, E. V.; Ageev, A. Yu.; Kutovoi, S. A.; Kuz'min, O. V. **X-ray diffraction study of the crystals LaSc₃(BO₃)₄ activated with chromium and neodymium ions.** Zhurnal Neorganicheskoi Khimii (1996), 41(10), 1605-1611.

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WE CLAIM:

1. A compound according to the formula $M_xM'_ySc_z(BO_3)_4$ where x, y,
5 and z sum to about four, and M and M' are selected from the group consisting of La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y.
2. The compound according to claim 1 having nonlinear optical
properties.
- 10 3. The compound according to claim 1 where M and M' are independently selected from the group consisting of Yb, Pr, Lu, and Y.
4. The compound according to claim 1 where if one of M or M' is Ce,
15 then the remaining metal is other than Gd or Nd.
5. The compound according to claim 1 where if one of M or M' is La, then the remaining metal is other than Nd, or x is greater than 0.3.
- 20 6. The compound according to claim 1 where M_x is La, and the compound further satisfies the formula $La_xM_ySc_z(BO_3)_4$ where each of x, y, and z is greater than zero, x, y and z sum to about four, and M_y is selected from the group consisting of rare earth metals if y is greater than 0.3, or is selected from the group of rare earth metals other than Nd, including La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er,
25 Tm, Yb, Lu, Sc and Y.
7. The compound according to claim 6 where M_y is selected from the group consisting of Y, Lu, Yb, and combinations thereof.
- 30 8. The compound according to claim 6 having a formula $La_{1-x}Y_xSc_3(BO_3)_4$ where x is greater than zero and less than one.

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9. The compound according to claim 8 where x varies from about 0.2 to about 0.4.
10. The compound according to claim 8 where x varies from about 0.25 to about 0.35.
11. The compound according to claim 1 crystallized in the R32 space group.
12. The compound according to claim 1 further satisfying the formula $\text{La}_{1-x}(\text{M}, \text{M}')_x\text{Sc}_3(\text{BO}_3)_4$ where x is greater than zero and less than one, and M and M' are independently selected from the group of rare earth metals.
13. The compound according to claim 12 where M and M' are independently selected from the group consisting of La, Pr, Gd, Dy, Ho, Er, Yb, Lu, Sc and Y.
14. The compound according to claim 12 where M and M' are independently selected from the group consisting of Yb, Pr, Lu, and Y.
15. A nonlinear optical material according to the formula $\text{La}_x\text{M}_y\text{Sc}_z(\text{BO}_3)_4$, where x, y, and z are greater than 0 and sum to about 4, and M_y is selected from the group consisting of Y, Lu, Yb, and combinations thereof.
16. The nonlinear optical material according to claim 15 where x is from about 0.7 to about 0.8.
17. The nonlinear optical material according to claim 15 where the material crystallizes in the space group R32.
18. A nonlinear optical material, $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$.

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19. A composition, comprising:
a first material according to the formula $M_xM'_ySc_z(BO_3)_4$, where x, y, and z sum to about four, and M and M' are selected from the group consisting of La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y; and
5 a second material.
20. The composition according to claim 19 where each of x, y, and z is greater than zero.
- 10 21. The composition according to claim 19 where the first material is operatively coupled to the second material.
22. The composition according to claim 19 where the first material is joined to the second material.
- 15 23. The composition according to claim 19 where the second material is a laser material or a nonlinear optical material.
24. The composition according to claim 19 where the second material
20 also satisfies the formula $M_xM'_ySc_z(BO_3)_4$, where M and M' independently are selected from the group consisting of the rare earth metals, x, y, and z are greater than zero, and x, y, and z sum to about four.
25. The composition according to claim 19 where M_x is La, and the
25 compound further satisfies the formula $La_xM_ySc_z(BO_3)_4$ where each of x, y, and z is greater than zero, x, y and z sum to about four, and M_y is selected from the group consisting of rare earth metals.
26. The composition according to claim 25 where y is greater than 0.3.
- 30 27. The composition according to claim 25 where M_y is selected from the group consisting of La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y.

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28. The composition according to claim 19 where the first material satisfies formula $\text{La}_{1-x}\text{Y}_x\text{Sc}_3(\text{BO}_3)_4$ where x is greater than zero and less than one.

29. The composition according to claim 28 where x varies from about 0.2
5 to about 0.4.

30. The composition according to claim 28 where x varies from about 0.25 to about 0.35.

10 31. The composition according to claim 19 where the first material is crystallized in the R32 space group.

32. The composition according to claim 19 where the first material further satisfies the formula $\text{La}_{1-x}(\text{Ln}, \text{Ln}')_x\text{Sc}_3(\text{BO}_3)_4$ where x is greater than zero and
15 less than one, and M and M' are independently selected from the group of rare earth metals.

33. A device for generating high energy UV light, comprising:
a laser; and
20 a nonlinear optical material having the formula $\text{M}_x\text{M}'_y\text{Sc}_z(\text{BO}_3)_4$ where x, y, and z sum to about four, and M and M' are selected from the group consisting of rare earth metals.

34. The device according to claim 33 where x, y and z each is greater
25 than zero.

35. The device according to claim 33 where, with reference to the nonlinear optical material, M_x is La, and the compound further satisfies the formula $\text{La}_x\text{M}_y\text{Sc}_z(\text{BO}_3)_4$ where each of x, y, and z is greater than zero, x, y and z sum to
30 about four, and M_y is selected from the group consisting of rare earth metals.

36. The device according to claim 35 where y is greater than 0.3.

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37. The device according to claim 35 where M_y is selected from the group of rare earth metals other than Nd, including La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y.

5 38. The device according to claim 33 having a formula $La_{1-x}Y_xSc_3(BO_3)_4$ where x is greater than zero and less than one.

39. The device according to claim 38 where x varies from about 0.2 to about 0.4.

10

40. The device compound according to claim 38 where x varies from about 0.25 to about 0.35.

41. The device according to claim 33 where the material is crystallized in
15 the R32 space group.

42. The device according to claim 33 where the material further satisfies the formula $La_{1-x}(M,M')_xSc_3(BO_3)_4$ where x is greater than zero and less than one, and M and M' are independently selected from the group of rare earth metals.

20

43. The device according to claim 42 where M and M' are independently selected from the group consisting of La, Pr, Gd, Dy, Ho, Er, Yb, Lu, Sc and Y.

44. The device according to claim 42 where M and M' are independently
25 selected from the group consisting of Y, Pr, Gd, Yb and Lu.

45. The device according to claim 33 where the material has a formula $La_xM_ySc_z(BO_3)_4$, where x, y, and z are greater than 0 and sum to about, and M_y is selected from the group consisting Y, Lu, Yb, and combinations thereof.

30

46. The device according to claim 45 where x is from about 0.7 to about 0.8.

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47. The nonlinear optical material according to claim 45 where the material crystallizes in the space group R32.

5 48. The device according to claim 33 where the material is $\text{La}_{0.7}\text{Y}_{0.3}\text{Sc}_3(\text{BO}_3)_4$.

49. A method for nonlinear generation of light, comprising:
providing a compound according to the formula $\text{M}_x\text{M}'_y\text{Sc}_z(\text{BO}_3)_4$ where x, y,
10 and z sum to about four, and M and M' are selected from the group consisting of La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y; and
exposing the compound to a light source.

50. The method according to claim 49 where M and M' are independently
15 selected from the group consisting of Y, Pr, Gd, Yb and Lu.

51. The method according to claim 49 where M_x is La, and the compound further satisfies the formula $\text{La}_x\text{M}_y\text{Sc}_z(\text{BO}_3)_4$ where each of x, y, and z is greater than zero, x, y and z sum to about four, and M_y is selected from the group consisting
20 of rare earth metals if y is greater than 0.3, or is selected from the group of rare earth metals other than Nd, including La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y.

52. The method according to claim 51 where M is selected from the
25 group consisting of Y, Lu, Yb, and combinations thereof.

53. The method according to claim 49 where the compound satisfies formula $\text{La}_{1-x}\text{Y}_x\text{Sc}_3(\text{BO}_3)_4$ where x is greater than zero and less than one.

30 54. The method according to claim 53 where x varies from about 0.2 to about 0.4.

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55. The method according to claim 53 where x varies from about 0.25 to about 0.35.

56. The method according to claim 49 where the compound is
5 crystallized in an R32 space group.

57. The method d according to claim 49 further satisfying the formula
 $\text{La}_{1-x}(\text{M}, \text{M}')_x \text{Sc}_3(\text{BO}_3)_4$ where x is greater than zero and less than one, and M and M'
are independently selected from the group of rare earth metals.
10

58. The method according to claim 49 where the material satisfies
formula $\text{La}_x \text{M}_y \text{Sc}_z (\text{BO}_3)_4$, where x, y, and z are greater than 0 and sum to about 4,
and M_y is selected from the group consisting Y, Lu, Yb, and combinations thereof.

15 59. A method according to claim 49 where the material is
 $\text{La}_{0.7} \text{Y}_{0.3} \text{Sc}_3 (\text{BO}_3)_4$.

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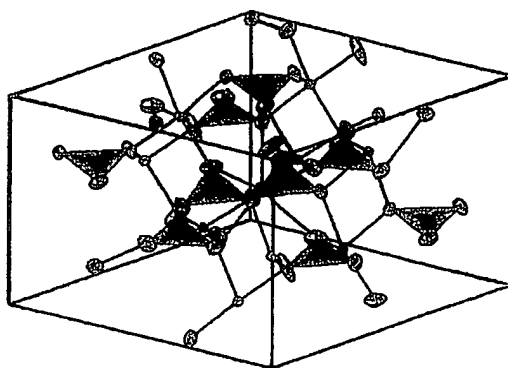


FIG. 1

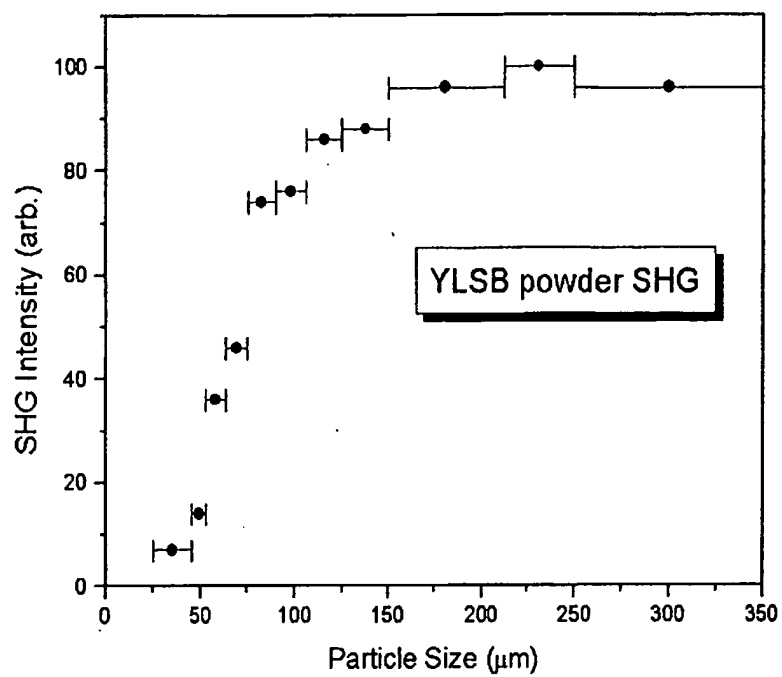


Figure 2. Phase-matching curve for YLSB

FIG. 2

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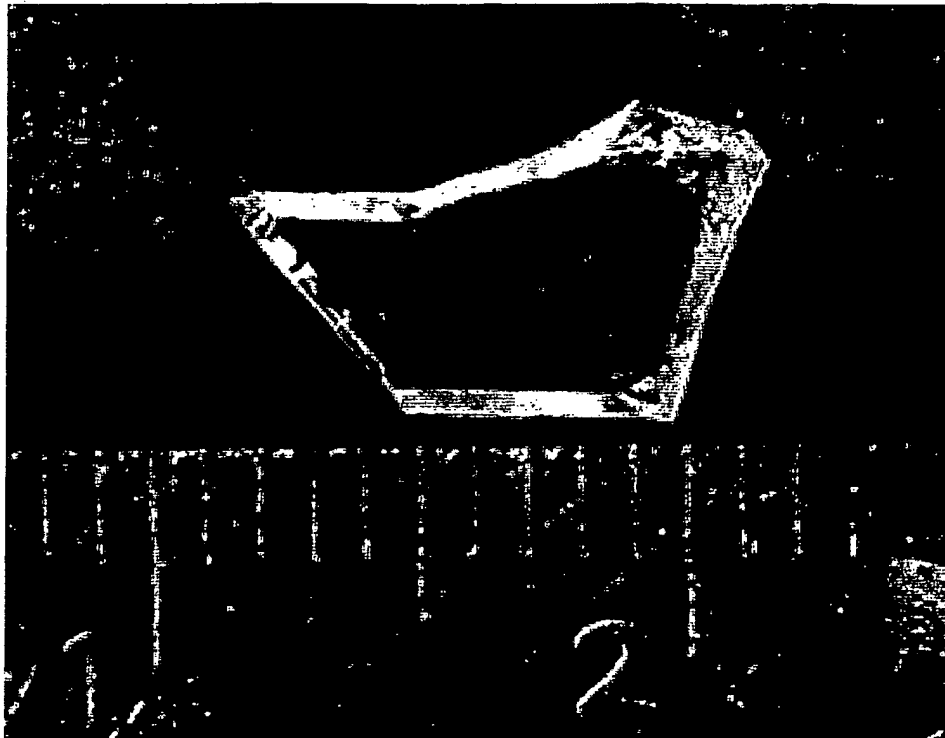


Figure 3. Polished YLSB crystal

FIG. 3

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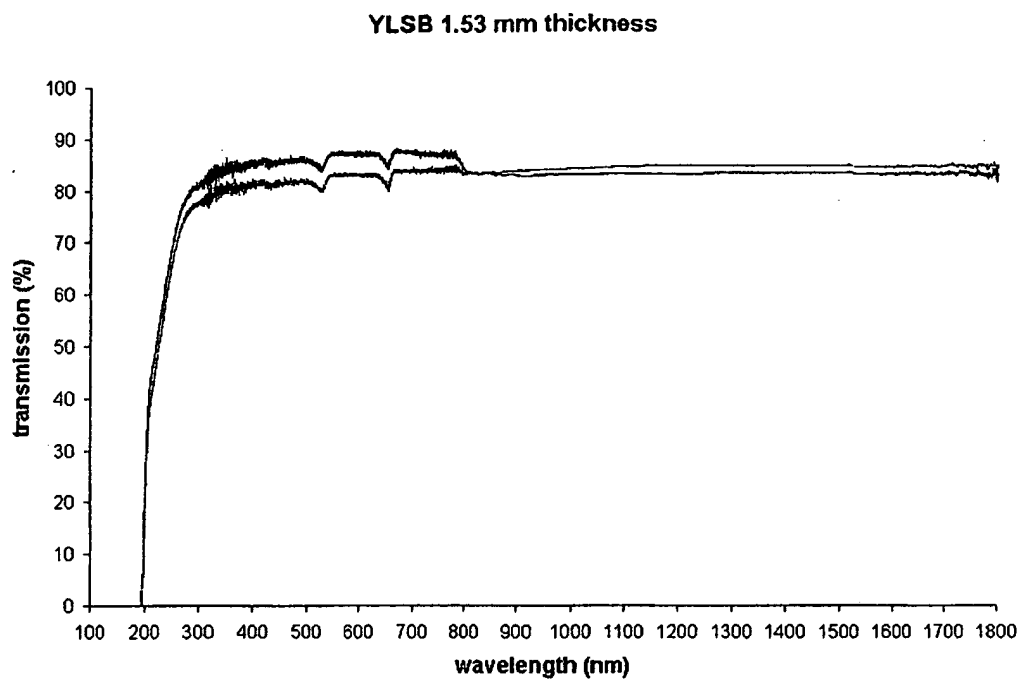


Figure 4. Transmission spectra for YLSB crystals

FIG. 4